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<p>(54) Title: <b>METHOD AND APPARATUS FOR ABSORBING HYDROGEN SULPHIDE</b></p>		
<p>(57) Abstract</p> <p>A method and an apparatus for selectively removing, by liquid absorption, hydrogen sulphide from a gas containing both hydrogen sulphide and carbon dioxide, are disclosed. In a first stage of the method, the gas (3) is in a container (1) contacted, in at least one step, with a carbonate-containing alkaline solution whose pH is adjusted during the absorption by the addition of a hydroxide, such as sodium hydroxide. In a second stage of the method, the gas is combusted in a combustion device (32) for converting the hydrogen sulphide remaining in the gas to sulphur dioxide, which then is absorbed in an alkali-containing solution, such as a sodium hydroxide solution, in a wet cleaner (36). By combining the absorption of hydrogen sulphide in a carbonate-containing solution in a first stage, and the combustion of the remaining hydrogen sulphide to sulphur dioxide and the absorption of the formed sulphur dioxide in an alkaline solution in a second stage, one may attain a total hydrogen-sulphide separation of high selectivity, high degree of separation and good process economy.</p>		

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# METHOD AND APPARATUS FOR ABSORBING HYDROGEN SULPHIDE

This invention relates to a method and an apparatus for absorbing hydrogen sulphide, more specifically a method and an apparatus for selectively removing, by liquid absorption, hydrogen sulphide from a gas containing both hydrogen sulphide and carbon dioxide.

- 5 It is well-known that hydrogen sulphide can be removed from hydrogen-sulphide-containing gases by being absorbed in an alkaline aqueous solution (i.e. an aqueous solution having a pH > 7), such as sodium hydroxide, or by using ethanolamine, such as monoethanol-  
10 amine and diethanolamine. Absorption may, for instance, be used for producing hydrogen sulphide in pure form, which optionally is further processed to sulphur in a Claus process. If the gas contains carbon dioxide in addition to hydrogen sulphide, the carbon dioxide will also be absorbed in the alkaline solution. Carbon dioxide has approximately the same solubility in water as hydrogen sulphide, and the carbon  
15 dioxide will therefore compete with the hydrogen sulphide for being absorbed in the solution. Hydrogen sulphide and carbon dioxide are absorbed in an alkaline aqueous solution of e.g. sodium hydroxide in accordance with the formulae below:

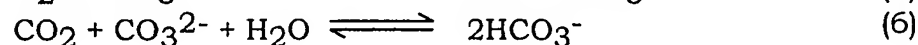
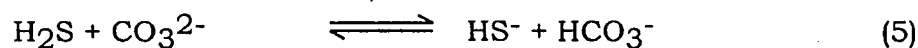


- 25 The selectivity to hydrogen sulphide, i.e. the ratio of mole of absorbed hydrogen sulphide to mole of absorbed (hydrogen sulphide + carbon dioxide), is directly proportional to the contents of hydrogen sulphide and carbon dioxide in the gas. Thus, the competition on the part of  
30 carbon dioxide is especially pronounced when the gas contains more carbon dioxide than hydrogen sulphide, as is mostly the case. If a gas contains, say, 1% by volume of hydrogen sulphide and 10% by volume of carbon dioxide and efforts are made to absorb the hydrogen sulphide in a sodium hydroxide solution, the selectivity to hydrogen sulphide is but 10%, i.e. 90% of the gas absorbed consists of carbon

phide is but 10%, i.e. 90% of the gas absorbed consists of carbon dioxide, which means that as much as 90% of the sodium hydroxide is spent in absorbing carbon dioxide.

In an effort to remedy the above inconvenience in the absorption of hydrogen sulphide from gases containing both hydrogen sulphide and carbon dioxide, methods for selective absorption of hydrogen sulphide have been developed. For instance, efforts have been made to selectively absorb hydrogen sulphide in solutions of strong oxidising agents, such as potassium permanganate, sodium dichromate or ferric salts. In other selective methods, use is made of alkaline solutions, such as sodium carbonate or potassium carbonate solutions, the operational conditions during the absorption being carefully adjusted. More detailed information about this prior-art technique is found in an article by C. Oloman, F.E. Murray and J.B. Risk entitled "The Selective Absorption of Hydrogen Sulphide from Stack Gas", Pulp and Paper Magazine of Canada, 5 December 1969, p. 69ff, as well as an article by E. Bendall, R.C. Aiken and F. Mandas entitled "Selective Absorption of H<sub>2</sub>S from Larger Quantities of CO<sub>2</sub> by Absorption and Reaction in Fine Sprays", AIChE Journal (Vol. 29, No. 1), January 1983, p. 66ff.

By using a carbonate solution, such as a sodium carbonate solution, instead of a hydroxide solution, such as a sodium hydroxide solution, the selectivity for the absorption of hydrogen sulphide can be augmented to about 30-50%. The reactions taking place during such an absorption can generally be rendered as follows:



When the absorption solution is a carbonate solution, the hydrogen sulphide is absorbed almost instantaneously, whereas the carbon dioxide reacts only slowly with the carbonate ions to form hydrogen carbonate ions. Owing to the high content of hydrogen carbonate generated when using a carbonate solution as absorption medium, there is the additional advantage of a "counterpressure" (equilibrium pressure) to the absorption of carbon dioxide, as appears from the equilibrium formula (6) above.

A problem that arises when using a carbonate solution as absorption medium is that only a fairly low hydrogen-sulphide content can be achieved in the solution, owing to the reduction of the absorption capacity caused by the formation of hydrogen carbonate ions. Thus, it is extremely difficult to attain hydrogen-sulphide contents exceeding about 10 g/l. As a result, prior-art methods for selectively absorbing hydrogen sulphide by means of an absorption medium in the form of a carbonate solution have not met with much success, despite the great demand for such a method in various fields where hydrogen-sulphide-containing and carbon-dioxide-containing gases are generated. Examples of such fields of application are petroleum refinement, coal-gas production and, in particular, the combustion of black liquor carried out in the sulphate pulp industry.

When recovering chemicals in the sulphate pulp industry in accordance with the conventional Tomlinson process, the black liquor is combusted in a soda recovery unit, resulting in the generation of steam and the formation of a melt chiefly consisting of sodium carbonate and sodium sulphide. The melt is then dissolved in water and causticised, so that the sodium carbonate is converted to sodium hydroxide and white liquor is obtained, which may then again be used for digesting wood. For many reasons, including the risk of an explosion when a tube in the soda recovery unit bursts, efforts have in recent years been made to develop new processes for the combustion of black liquor, in which no melt is formed. Such processes can be collectively referred to as "black-liquor evaporation", and one instance thereof is the so-called SCA-Billerud process (E. Hornstedt and J. Gomy, Paper Trade Journal 158 (1974):16, pp 32-34). In this process, the black liquor is pyrolysed in a reactor under such temperature conditions that dust, which chiefly consists of sodium carbonate and carbon, and a combustible gas, which inter alia contains sulphur compounds, are formed. Another instance of black-liquor evaporation is given in Swedish Patent Application 8605116-0, which concerns a method for thermal decomposition of black liquor with concurrent supply of oxygen in an amount short of the stoichiometrically required amount, at a pressure above 10 bar, and at such a temperature that no melt is formed. The evaporation results in the formation of a solid phase, which chiefly consists of sodium carbonate, and a gaseous

phase, which chiefly consists of hydrogen sulphide, carbon monoxide, carbon dioxide, hydrogen, water vapour, and methane.

In order to be able to recover the chemicals used in black-liquor evaporation as above and produce from these chemicals white liquor to be used in the manufacture of pulp, it is necessary that the hydrogen sulphide can be removed from the generated gas. Since the gas also contains carbon dioxide, the latter will compete with the hydrogen sulphide in the liquid absorption, and since the gas has a low content of hydrogen sulphide (about 0.5-2%) and a carbon dioxide content that is some 20 times higher (about 10-20%), conventional liquid absorption results in unsatisfactory recovery of hydrogen sulphide.

There is thus a need to be able to separate, by liquid absorption, the hydrogen sulphide with a high degree of separation and a high degree of selectivity from gases containing both hydrogen sulphide and carbon dioxide.

According to Swedish Patent Application 9300533-8, which was filed on 18 February 1993 but has not yet been published, it has been found that absorption with a high degree of separation of hydrogen sulphide and a high degree of selectivity for hydrogen sulphide can be obtained by using, as a liquid absorption medium, a carbonate-containing alkaline solution and adjusting the pH of the solution during the absorption of hydrogen sulphide by the addition of a hydroxide, i.e. not by the addition of fresh carbonate. Thus, it is possible to obtain a selectivity for hydrogen sulphide in the absorption of 60-70%, a sulphide content in the absorption solution of about 30 g/l, and a degree of separation of hydrogen sulphide of about 90-99%.

To be more precise, this is attained by a method which is of the type stated by way of introduction and in which the gas is contacted in at least one step with a carbonate-containing alkaline solution whose pH is adjusted during the absorption by the addition of a hydroxide.

The inventive method can be implemented with the aid of an apparatus, which is characterised in that it comprises: a container having a gas inlet and a gas outlet and containing a packing arranged in a number of successive steps; means for supplying a carbonate-

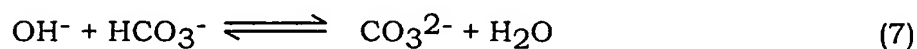
containing solution to the last step, as seen in the feed direction of the gas, each step having means for supplying the carbonate-containing solution through the step countercurrently to the gas and for recycling the solution over the step; conduits arranged between the steps for supplying a partial flow of the solution from one step to a preceding step, as seen in the feed direction of the gas; means for supplying a hydroxide to the carbonate-containing solution in at least one of the steps; and an outlet conduit from the first step, as seen in the feed direction of the gas, for discharging liquid containing hydrogen sulphide.

By "carbonate-containing alkaline solution" is meant an aqueous solution containing carbonate ions ( $\text{CO}_3^{2-}$ ). Preferably, this solution is an alkali metal carbonate solution, such as a solution of sodium carbonate, potassium carbonate or lithium carbonate. Sodium carbonate is especially preferred, being easily accessible as well as fairly inexpensive. The carbonate concentration of the solution is not critical, but conveniently is about 0.1-3 M with respect to carbonate, preferably about 1-2.5 M, and most preferred about 1.7 M.

It is essential that the carbonate-containing alkaline solution has a pH of at least about 9. pH values below about 9 result in unsatisfactory absorption of hydrogen sulphide, and there is even a risk that hydrogen sulphide already absorbed be released from the solution. However, the pH of the solution should not be too high, since this would have an adverse effect on the absorption of hydrogen sulphide, as compared with that of carbon dioxide. Thus, the pH of the solution should preferably not exceed about 12 in order that the absorption of carbon dioxide should not be too considerable. Preferably, the pH of the solution is in the range of about 10.0-11.0, and most preferred in the range of about 10.2-10.8. If the pH of the solution is adjusted within this last narrow range, optimum separation of hydrogen sulphide is obtained.

As appears from the equilibrium reactions (5) and (6), hydrogen carbonate ions ( $\text{HCO}_3^-$ ) are formed in the absorption of hydrogen sulphide and carbon dioxide. This means that the pH of the absorption solution decreases as the absorption of hydrogen sulphide and carbon dioxide proceeds. When the pH of the solution goes below about 9, the absorption of hydrogen sulphide becomes unsatisfactory, as indicated

in the foregoing, and there is instead a risk that hydrogen sulphide already absorbed be released from the solution. If this is to be avoided, the solution has to be regenerated, i.e. its pH be increased to above the lower permissible limit for a state of equilibrium between gaseous H<sub>2</sub>S and sulphide content of the liquid at the temperature and pH value at issue. However, the pH value must not be increased to above about 12, in which case the absorption of carbon dioxide would become predominant. As a result of the increase of the pH of the solution brought about by the addition of a hydroxide, such as an alkali metal hydroxide, e.g. NaOH, the hydrogen carbonate ions formed are reconverted to carbonate ions according to the following equilibrium reaction:



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Being thus regenerated, the carbonate solution can absorb more hydrogen sulphide according to the reaction (5) above. Since the pH of the solution is adjusted by the addition of a hydroxide and maintained within the given range of about 9-12, preferably about 10.0-11.0, and most preferred about 10.2-10.8, the absorption of carbon dioxide is kept on a comparatively low level.

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As indicated in the foregoing, the carbonate-containing alkaline solution is regenerated by the addition of a hydroxide. Basically, use can be made of any hydroxide that does not have an adverse effect on the absorption of hydrogen sulphide and is capable of increasing the pH of the solution from the given lower limit of about 9 to the desired value, such as a value not exceeding about 12.0, preferably not exceeding about 11.0, and most preferred not exceeding about 10.8. According to the invention, use is preferably made of hydroxides of alkali metals or alkaline-earth metals, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (LiOH), calcium hydroxide (Ca(OH)<sub>2</sub>), and magnesium hydroxide (Mg(OH)<sub>2</sub>). For reasons of availability and cost, sodium hydroxide is most preferred.

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The temperature of the liquid used in the absorption is not particularly critical and may vary within a wide range, but preferably is below about 80°C, since there is a risk that the absorption of hydrogen sulphide decreases at temperatures of about 80°C and above. It

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is preferred that the temperature is in the range of from room temperature, i.e. about 20°C, to about 80°C, more preferably about 40-70°C, and most preferred about 60-70°C.

In order to optimise the selectivity to hydrogen sulphide in the liquid absorption, the absorption should be carried out in such a manner that the flow of gas and the flow of absorbing liquid are counter-current, and the flow of gas should be turbulent and the flow of liquid laminar. Moreover, the separation of hydrogen sulphide is promoted if the volume of absorbing liquid is large compared with the volume of gas from which hydrogen sulphide is absorbed. Such a high ratio of liquid to gas is achieved by recycling the absorbing liquid that is contacted with the hydrogen-sulphide-containing gas.

Furthermore, the contact between the sulphur-containing gas and the absorbing liquid (the carbonate-containing solution) may involve one or more steps, preferably two or three steps, and most preferred three steps. Such multistep contact has the advantage of shortening the length of each individual step, such that the pH of the carbonate-containing solution does not have time to fall below about 9 in the individual step, while at the same time the sulphide content can be kept low in the uppermost step. Preferably, each step has such an extent or length that the pH of the solution at the end of the step has fallen to about 10.0-10.2, the liquid being then drawn off to be regenerated by means of a hydroxide and then recycled to the step at issue.

According to the invention, it has been found that the removal of hydrogen sulphide in a method of the above type can be rendered more efficient, while drastically reducing the chemical consumption, if the method is divided into two stages, namely a first stage, in which the main part of the hydrogen sulphide is removed in accordance with the method described above, and a second stage, in which the remaining hydrogen sulphide is essentially removed by combustion to sulphur dioxide, which is absorbed in an alkaline solution in a wet cleaner (scrubber). The reason for this is as follows.

As hydrogen sulphide is absorbed in the different steps of the first stage, the hydrogen-sulphide content of the gas decreases, which results in a reduction of the previously-defined selectivity to hydrogen sulphide. When the selectivity is reduced, the consumption of alkali

increases dramatically in accordance with the reactions (5), (6) and (7) indicated above. As appears from these reactions, 1 mole of  $\text{OH}^-$  is spent per mole of hydrogen sulphide absorbed, and 2 mole of  $\text{OH}^-$  is spent per mole of carbon dioxide absorbed. When the selectivity to hydrogen sulphide is reduced and the absorption of carbon dioxide increases, as is the case in the last absorption step or steps of the first stage, the consumption of alkali ( $\text{OH}^-$ ) increases considerably. This means that it takes a comparatively larger amount of alkali to absorb the "last" hydrogen sulphide of the gas than to absorb the "first" hydrogen sulphide of the gas. By refraining from carrying the absorption of hydrogen sulphide to the full in the first stage, but purposely leaving a certain amount of hydrogen sulphide in the gas discharged from the first stage, one avoids that the selectivity to hydrogen sulphide is dramatically reduced and, consequently, that the consumption of alkali increases dramatically in the first stage. The hydrogen-sulphide absorption in the first stage is so carried out that the main part of the hydrogen sulphide, i.e. at least 50%, is removed. Conveniently, about 60-97%, preferably about 80-95%, and most preferred about 90%, of the hydrogen sulphide is removed in the first stage. This results in a low consumption of alkali in the first stage, which involves good process economy.

Before the gas from the first stage can be let out into the surrounding atmosphere, the remaining hydrogen sulphide must, however, be removed. According to the invention, this takes place by combusting the hydrogen-sulphide-containing gas from the first stage, such that the hydrogen sulphide is oxidised to sulphur dioxide, whereupon the sulphur dioxide formed is absorbed in an aqueous solution, whose pH is adjusted by the addition of an alkaline solution or an alkaline substance, in a wet cleaner (scrubber).

The present invention thus provides a method for selectively removing, by liquid adsorption, hydrogen sulphide from a gas containing both hydrogen sulphide and carbon dioxide, characterised in that the gas, in a first stage for removing the main part of the hydrogen-sulphide content of the gas, is contacted in at least one step with a carbonate-containing alkaline solution whose pH is adjusted during the absorption by the addition of a hydroxide, and that the gas is then in a second stage combusted in order to convert the remaining hydro-

gen sulphide to sulphur dioxide, which is absorbed in an alkali-containing solution.

The invention further provides an apparatus for selectively removing, by liquid absorption, hydrogen sulphide from a gas containing both hydrogen sulphide and carbon dioxide, characterised in that it comprises

- a) a container having a gas inlet and a gas outlet and containing a packing arranged in a number of successive steps; means for supplying a carbonate-containing solution to the last step, as seen in the feed direction of the gas, each step having means for supplying the carbonate-containing solution through the step countercurrently to the gas and for recycling the solution over the step; conduits arranged between the steps for supplying a partial flow of the solution from one step to a preceding step, as seen in the feed direction of the gas;
- means for supplying a hydroxide to the carbonate-containing solution in at least one of the steps; and an outlet conduit from the first step, as seen in the feed direction of the gas, for discharging liquid containing hydrogen sulphide,
- b) a combustion device having an inlet for hydrogen-sulphide-containing gas from the gas outlet of the container; combustion means for combusting the gas supplied and converting the hydrogen sulphide therein to sulphur dioxide; and an outlet for discharging sulphur-dioxide-containing gas from the combustion device, and
- c) a wet cleaner adapted to absorb the sulphur dioxide formed upon combustion, and comprising a container which has an inlet for sulphur-dioxide-containing gas from the combustion device; an outlet for cleaned gas; means for supplying, circulating and finely dividing an aqueous solution, whose pH is adjusted by the addition of alkaline solution or alkaline substance, so as to contact it with the sulphur-dioxide-containing gas supplied; and means for discharging the solution that has absorbed sulphur dioxide.

Further distinctive features of the invention appear from the following description and are stated in the appended claims.

As indicated in the foregoing, the carbonate-containing alkaline solution used in the first stage for hydrogen-sulphide absorption is an aqueous solution containing carbonate ions, such as a solution of alkali metal carbonate, preferably sodium carbonate. When the inven-

tive method is used for removing hydrogen sulphide in the sulphate pulp industry, for instance when combusting black liquor, one has found that green liquor may be used as the carbonate-containing alkaline solution according to the invention, and this constitutes a particular aspect of the invention. Green liquor is an aqueous solution that usually contains about 1.3-1.4 mole of  $\text{Na}_2\text{CO}_3$  per litre, about 0.4-0.6 mole of  $\text{Na}_2\text{S}$  per litre, and about 0.3-0.5 mole of  $\text{NaOH}$  per litre. According to the invention, it has also been found that white liquor may likewise be used in the first stage as the hydroxide for regenerating the carbonate-containing alkaline solution, when the invention is employed in the sulphate pulp industry for removing hydrogen sulphide. White liquor is an aqueous solution that contains  $\text{NaOH}$ ,  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{CO}_3$ , usually in the proportions of about 2.3-2.6 mole of  $\text{NaOH}$  per litre, about 0.4-0.6 mole of  $\text{Na}_2\text{S}$  per litre, and about 0.25-0.4 mole of  $\text{Na}_2\text{CO}_3$  per litre. Also the use of white liquor as the hydroxide for regenerating the carbonate-containing alkaline solution constitutes a particular aspect of the invention.

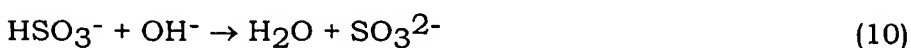
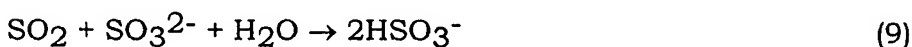
Instead of white liquor, use can be made of weak liquor or oxidised white liquor for regenerating the carbonate-containing alkaline solution. By weak liquor is meant an aqueous solution that contains  $\text{NaOH}$ ,  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{CO}_3$ , usually in the proportions of about 0.3-0.4 mole of  $\text{NaOH}$  per litre, about 0.05-0.08 mole of  $\text{Na}_2\text{S}$  per litre, and about 0.05-0.07 mole of  $\text{Na}_2\text{CO}_3$  per litre.

Since green liquor, white liquor as well as weak liquor contain both carbonate and hydroxide, they may be used either separately or together, both as the carbonate-containing solution and for regenerating the carbonate-containing alkaline solution.

In the second stage, the combustion of the hydrogen-sulphide-containing gas takes place in known manner in a combustion device of known type, such as a lime sludge reburning kiln or a bark burning boiler when the invention is used in the sulphate pulp industry. If the heat content of the hydrogen-sulphide-containing gas is too low, an auxiliary fuel, such as oil or natural gas, may be used in the combustion to produce satisfactory oxidation of the hydrogen sulphide to sulphur dioxide. When the hydrogen-sulphide-containing gas is burnt, the hydrogen sulphide is, at normal combustion temperatures,

completely oxidised to sulphur dioxide, and the gas thus contains only negligible amounts of hydrogen sulphide after the combustion.

After the combustion of the hydrogen-sulphide-containing gas in the second stage, the sulphur dioxide formed should be removed, which according to the invention takes place by it being absorbed in an alkali-containing solution in a wet cleaner (scrubber). To selectively remove, by absorption in an alkali-containing solution in a scrubber, sulphur dioxide from a gas which in addition contains carbon dioxide, is a well-known technique, which need not be described in more detail here. Conveniently, use is made of a scrubber where the absorbing alkali-containing solution is recycled to a high extent. The pH of the alkali-containing solution in the SO<sub>2</sub> scrubber is preferably in the range of about 6-8, and most preferred in the range of about 7-7.5. At these fairly low pH values, the absorption of carbon dioxide is negligible, and the selectivity to the sulphur-dioxide separation consequently is 100%. During the absorption, the sulphur dioxide undergoes one of the following reactions:



As appears from the reaction formulae (8)-(10), 2 mole of OH<sup>-</sup> is spent per mole of SO<sub>2</sub> absorbed. Since no carbon dioxide is absorbed, the absorption of sulphur dioxide can be carried out to almost 100% of the sulphur dioxide present without there being any noticeable increase in the alkali consumption. This considerably improves process economy, as compared with the case when all the sulphur is absorbed as hydrogen sulphide in the first stage, which results in poor selectivity.

The alkali in the alkali-containing solution conveniently is a hydroxide or a carbonate of an alkali metal or an alkaline-earth metal, such as sodium hydroxide, potassium hydroxide, calcium carbonate, calcium hydroxide or magnesium hydroxide. Sodium hydroxide is preferred, especially if the sulphur is to be recycled directly in the pro-

cess, e.g. when the method is employed in the sulphate pulp industry. If so, use is conveniently made of a sodium-hydroxide-based spray scrubber, for instance of the type used by ABB Fläkt Industri AB and designated the MoDo scrubber. The scrubber may then comprise one  
5 or more heat-recovery steps, in which cold water is sprayed towards the hot gas, so that hot water having a temperature of about 45-65°C is obtained. After the absorption of sulphur dioxide, the solution leaving the scrubber contains sodium sulphite ( $\text{Na}_2\text{SO}_3$ ), sodium hydrogen sulphite ( $\text{NaHSO}_3$ ) and sodium sulphate ( $\text{Na}_2\text{SO}_4$ ). In the sulphate pulp industry, this solution can be mixed with other combustible process liquids, e.g. the black liquor in a pulp mill. A combustion under reducing conditions results in sulphur in the form of hydrogen sulphide, and a combustion under oxidising conditions results in sulphur in the form sulphur dioxide.

15 In the pulp industry, the method according to the invention is conveniently so designed that its different stages are integrated in the existing equipment. This means that the combustion of the hydrogen-sulphide-containing gas takes place in an existing bark burning boiler or lime sludge reburning kiln. This reduces the need for other fuels in  
20 these process steps. The sulphur-dioxide-containing flue gases from the bark burning boiler or the lime sludge reburning kiln can then be conducted to an existing  $\text{SO}_2$  scrubber. In this case, the only new equipment needed is a scrubber for the separation of hydrogen sulphide.

25 Pulp mills may be equipped with separate  $\text{SO}_2$  scrubbers for flue gases from the bark burning boiler and the lime sludge reburning kiln and from the soda recovery boiler, respectively. When the hydrogen-sulphide-containing gas is combusted elsewhere, for example in a separate boiler, the sulphur-dioxide-containing flue gases can be conducted to the existing  $\text{SO}_2$  scrubber for the flue gases from the soda  
30 recovery boiler.

It is evident from the foregoing that the present invention enables good process economy, a closed chemical system in which all the sulphur is recycled, as well as very low emissions to the surrounding atmosphere.  
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For clarifying purposes, the invention will now be described in more detail with reference to the accompanying drawings, in which

Fig. 1 shows a preferred apparatus according to the invention for implementing the first stage of the method according to the invention; and

Fig. 2 is a schematic flow chart illustrating the method according to the invention.

The apparatus shown in Fig. 1 comprises a tower or container 1 having an inlet 2 for a gas 3 which contains hydrogen sulphide as well as carbon dioxide. At the opposite end of the apparatus, there is provided an outlet 4 for gas 5 from which hydrogen sulphide has been removed by liquid absorption. The contact between the hydrogen-sulphide-containing gas and the carbonate-containing solution involves three steps 6, 7 and 8. Each step contains a packing 9, as hinted at in step 6 in the Figure. In order to optimise the selectivity to hydrogen sulphide in the absorption, the packing 9 has such a shape as to generate a laminar flow of liquid through the steps 6, 7 and 8. It has been found that a packing in the form of corrugated plates is especially suitable for this purpose. The packing may, for instance, be made of plastic or metal.

The contact between the hydrogen-sulphide-absorbing, carbonate-containing solution and the hydrogen-sulphide-containing gas is carried out in countercurrent fashion. To this end, each step has means for supplying the carbonate-containing solution through the step countercurrently to the gas, as well as for recycling the solution over the step. As shown in Fig. 1, these means are made up of pumps 10, 11 and 12 which, via conduits 13, 14 and 15, feed the carbonate-containing alkaline solution to the respective steps 6, 7 and 8, as well as conduits 16, 17 and 18 which conduct the solution from the respective steps to collecting vessels 19, 20 and 21. From these collecting vessels, the solution is recycled over the steps through conduits 22, 23 and 24, which are connected to the pumps 10, 11 and 12, respectively. Fresh carbonate solution, preferably sodium carbonate solution, is fed to the last step 6, as seen in the feed direction of the gas, through a conduit 25 from a supply (not shown) of sodium carbonate solution.

Instead of supplying fresh carbonate solution to the last step, the carbonate solution can be generated in the last step by supplying sodium hydroxide solution to this step and allowing the hydroxide

solution to absorb carbon dioxide from the gas, such that a carbonate-containing solution is obtained according to the reactions (3)-(4) above.

In order to adjust (increase) the pH of the absorption solution, a hydroxide, preferably a sodium hydroxide solution, may be supplied to the collecting vessels 19, 20 and 21 through conduits 26, 27 and 28, respectively, conducting alkali from a supply (not shown), which preferably is common to all the conduits. The supply of sodium hydroxide solution for adjusting the pH of the absorption solution is regulated on the basis of the measured pH values of the solutions in the collecting vessels 19, 20 and 21 (not shown).

As appears from Fig. 1, the different steps are further interconnected by conduits 29 and 30 for feeding a partial flow of the absorption solution from one step to the preceding step, i.e. from the step 6 to the step 7 as well as from the step 7 to the step 8.

Finally, an outlet conduit 31 is arranged for discharging hydrogen-sulphide-containing liquid from the collecting vessel 21 and the step 8.

Fig. 2 is a schematic flow chart illustrating the method according to the invention. As indicated in the flow chart, a hydrogen-sulphide-containing and carbon-dioxide-containing gas 3 is, in a first stage, treated in an apparatus which includes a container 1 for the absorption of hydrogen sulphide, as described in the foregoing with reference to Fig. 1. According to the invention, the absorption of hydrogen sulphide is not, in the first stage, carried out to 100%, i.e. total absorption of hydrogen sulphide in the first stage, but only so far that at least the main part of the hydrogen sulphide, i.e. at least 50%, preferably about 60-97%, more preferably about 80-95% and most preferred about 90%, of the hydrogen sulphide is absorbed in the first stage. Preferably, a total of at least about 98% of the hydrogen-sulphide content of the gas is absorbed by the first and the second stage.

The thus-cleaned gas 5, which still contains hydrogen sulphide and carbon dioxide, is then fed from the first stage to the second stage, in which the gas is first combusted in order to convert hydrogen sulphide to sulphur dioxide, and then wet-cleaned in a scrubber in view of the absorption of the sulphur dioxide formed.



As indicated in Fig. 2, the combustion takes place in a combustion device 32, which has combustion means 33, e.g. a burner, for combusting the gas 5 supplied through an inlet 34 and oxidising the hydrogen sulphide to sulphur dioxide. As mentioned in the foregoing, the combustion device 32 may consist of existing equipment, such as a bark burning boiler or a lime sludge reburning kiln. The sulphur-dioxide-containing flue gas is discharged through an outlet 35 and conducted to a wet cleaner 36, which comprises a container 37 having an inlet 38 for the sulphur-dioxide-containing gas, an outlet 39 for the cleaned gas 40, and means 41 for supplying an alkali-containing solution. As mentioned above, the alkali-containing solution contains a hydroxide of an alkali metal or alkaline-earth metal, preferably sodium hydroxide. The solution is circulated by means of a pump 42 to nozzles 43, where it is finely divided and is countercurrently brought into contact with the sulphur-dioxide-containing gas, such that the sulphur dioxide is absorbed by the solution. In order to optimise the absorption of sulphur dioxide, without any competing absorption of carbon dioxide, the pH of the solution is adjusted to about 6-8, preferably 7-7.5. The solution that has absorbed sulphur dioxide is discharged from the second stage at 44.

The invention will now be further elucidated with the aid of a non-restricting Example.

#### Example

A test was performed for the selective removal of hydrogen sulphide from a gas generated in black-liquor evaporation. Use was made of an apparatus of the type described above and shown in Figs 1 and 2.

In the first stage of the method, the absorption of hydrogen sulphide took place at atmospheric pressure, and the feed gas had a temperature of about 60°C and contained 1.13 mole % of hydrogen sulphide and 16.9 mole % of carbon dioxide. The gas was saturated with water vapour at the temperature at issue, which corresponded to about 18.7 mole % of water. The feed gas flow was 38280 Nm<sup>3</sup>/h, giving the gas a velocity of about 3.1 m/s in the absorption tower. The absorption tower had a height of 6.25 m, and the two first steps each had a height of 1.5 m, whereas the last step, as seen in the feed direction of the gas, had a height of 1 m. Each step was provided with

a packing of the type Mellapack 500 from Sulzer. The diameter of the tower was 2.3 m.

Fresh absorption solution, which consisted of 8.8 m<sup>3</sup>/h of 2 M sodium carbonate solution having a temperature of about 60°C, was supplied to the last step in the tower along with recycled absorption solution, such that a total of about 50 m<sup>3</sup>/h of absorption solution was supplied to the last step in the tower. The pH of the absorption solution supplied was about 11.0, which was reduced to about 10.2 during the passage of the solution through the step owing to the absorption of hydrogen sulphide. After passing through the step, the solution was supplied to a 1.5 m<sup>3</sup> collecting vessel, where the solution was regenerated by the addition of a 2.5 M sodium hydroxide solution having a temperature of about 60°C, such that the pH of the solution was again increased to about 11.0. Then, the regenerated solution was recycled by means of a pump to the last step in the absorption tower for renewed absorption of hydrogen sulphide.

About 11 m<sup>3</sup>/h of the absorption solution was drawn off from the collecting vessel to the collecting vessel of the intermediate step, whence about 50 m<sup>3</sup>/h of the absorption solution having a pH of about 11.0 was pumped, as in the previous step, to the intermediate step, whence the absorption solution was drawn off at a pH of about 10.2 to be recycled to the collecting vessel. In the collecting vessel, the solution was regenerated by the addition of a 2.5 M sodium hydroxide solution having a temperature of about 60°C, as in the previous step.

From the collecting vessel of the intermediate step, about 13.5 m<sup>3</sup>/h of the absorption solution was drawn off to the collecting vessel of the first (lowermost) step, whence 50 m<sup>3</sup>/h of the absorption solution having a pH of about 11.0 was pumped to the first step, as seen in the feed direction of the gas. After passing this step and there absorbing hydrogen sulphide, the solution, now having a pH of about 10.2, was drawn off to be recycled to the collecting vessel. In the collecting vessel, the solution was regenerated as in the previous steps by the addition of a 2.5 M sodium hydroxide solution having a temperature of about 60°C, such that the pH of the regenerated solution was about 11.0. All in all, about 8.6 m<sup>3</sup>/h of the 2.5 M sodium hydroxide solution was added to the collecting vessels of the three steps.

From the collecting vessel of the first (lowermost) step, about 17.4 m<sup>3</sup>/h of the solution having a HS<sup>-</sup> concentration of 1 mole/l was drawn off. The gas leaving the absorption tower contained 0.113 mole % of hydrogen sulphide and 16.4 mole % of carbon dioxide. In the first stage of the method, the degree of separation of hydrogen sulphide was about 90%, and the selectivity to hydrogen sulphide in the separation was about 0.67%.

Then came the second stage of the method. Thus, the gas leaving the absorption tower in the first stage was combusted in a furnace to which was added 31700 Nm<sup>3</sup>/h of air, which resulted in 66000 Nm<sup>3</sup>/h of flue gas containing 650 ppm of SO<sub>2</sub> (1930 mole/h). This flue gas was conducted to an SO<sub>2</sub> scrubber of conventional type described in the foregoing. In the scrubber, 1.54 m<sup>3</sup>/h of the 2.5 M sodium hydroxide solution was spent, and 2.0 m<sup>3</sup>/h of fresh water was in addition supplied to the scrubber in order to cool the incoming flue gas to saturation temperature. The gas leaving the scrubber had an SO<sub>2</sub> concentration of 12 ppm, which corresponded to 35 mole/h (1.12 kg/h of sulphur). The supplied absorption solution was kept at a constant pH of 7.2. The absorption solution was recycled in the scrubber at a total flow rate of 170 m<sup>3</sup>/h. From the scrubber was drawn off 1.8 m<sup>3</sup>/h of the solution, which had a total sulphur concentration (SO<sub>3</sub><sup>2-</sup> + HSO<sub>3</sub><sup>-</sup> + SO<sub>4</sub><sup>2-</sup>) of 1.05 mole/l. The total degree of separation of sulphur, i.e. the degree of separation of hydrogen sulphide in the first stage plus the degree of separation of sulphur dioxide in the second stage, thus was 99.8%. In the first stage, 860 kg/h of sodium hydroxide was spent, and in the second stage, 152 kg/h of sodium hydroxide was spent, i.e. a total of 1012 kg/h of NaOH was spent in order to obtain a degree of separation of sulphur of 99.8%.

For comparative purposes, the method was repeated, but this time only with the first stage, i.e. the combustion of hydrogen sulphide to sulphur dioxide and the absorption of the formed sulphur dioxide in a wet scrubber were not performed. Instead, the separation of hydrogen sulphide in the first stage was carried out to such an extent that 98% of the hydrogen sulphide was separated. The selectivity to hydrogen sulphide in a 90-98% separation of hydrogen sulphide is 0.15. The total selectivity for the whole stage then is about

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NaOH consumption more than 70% higher than in the inventive method, despite the fact that the total degree of separation of sulphur was lower.

## CLAIMS

1. A method for selectively removing, by liquid absorption,  
5 hydrogen sulphide from a gas (3) containing both hydrogen sulphide and carbon dioxide, c h a r a c t e r i s e d in that the gas (3), in a first stage for removing the main part of the hydrogen-sulphide content of the gas, is contacted in at least one step (6, 7, 8) with a carbonate-containing alkaline solution (25) whose pH is adjusted during  
10 the absorption by the addition of a hydroxide (26, 27, 28), and that the gas is thereafter combusted in a second stage in order to convert the remaining hydrogen sulphide to sulphur dioxide, which is absorbed in an aqueous solution whose pH is adjusted by the addition of alkaline solution or alkaline substance.
- 15 2. A method as claimed in claim 1, c h a r a c t e r i s e d in that the gas (3), in said first stage, is contacted with a solution (25) containing sodium carbonate.
3. A method as claimed in claim 2, c h a r a c t e r i s e d in that the gas (3) is contacted with green liquor, white liquor or weak  
20 liquor, especially green liquor.
4. A method as claimed in claim 1, c h a r a c t e r i s e d in that the pH of the carbonate-containing alkaline solution is adjusted in said first stage by means of a liquid (26, 27, 28) containing alkali metal hydroxide.
- 25 5. A method as claimed in claim 4, c h a r a c t e r i s e d in that the pH is adjusted by means of white liquor, green liquor or weak liquor, preferably white liquor or weak liquor, especially white liquor.
6. A method as claimed in any one of the preceding claims,  
30 c h a r a c t e r i s e d in that the gas, in said first stage, is contacted with the carbonate-containing solution (25) at a pH of about 9-12, preferably about 10-11.
7. A method as claimed in any one of the preceding claims, c h a r a c t e r i s e d in that the gas, in said second stage after  
35 the combustion, is absorbed in the aqueous solution at a pH of about 6-8, preferably about 7.0-7.5.

8. A method as claimed in any one of the preceding claims, characterised in that about 60-97%, preferably about 80-95%, of the hydrogen-sulphide content of the gas is removed in the first stage.

5 9. A method as claimed in any one of the preceding claims, characterised in that in all at least about 98% of the hydrogen-sulphide content of the gas is removed.

10 10. An apparatus for selectively removing, by liquid absorption, hydrogen sulphide from a gas (3) containing both hydrogen sulphide and carbon dioxide, characterised in that it comprises  
a) a container (1) having a gas inlet (2) and a gas outlet (4) and containing a packing (9) arranged in a number of successive steps (6, 7, 8); means (25) for supplying a carbonate-containing solution to the last step, as seen in the feed direction of the gas, each step having  
15 means for supplying the carbonate-containing solution through the step countercurrently to the gas and for recycling the solution over the step; conduits (29, 30) arranged between the steps for supplying a partial flow of the solution from one step to a preceding step, as seen in the feed direction of the gas; means (26, 27, 28) for supplying  
20 a hydroxide to the carbonate-containing solution in at least one of the steps (6, 7, 8); and an outlet conduit (31) from the first step, as seen in the feed direction of the gas, for discharging liquid containing hydrogen sulphide,

b) a combustion device (32) having an inlet (34) for hydrogen-sulphide-containing gas (5) from the gas outlet (4) of the container (1), combustion means (33) for combusting the gas supplied and converting the hydrogen sulphide therein to sulphur dioxide, and an outlet (35) for discharging sulphur-dioxide-containing gas from the combustion device (32), and

30 c) a wet cleaner (36) adapted to absorb the sulphur dioxide formed upon combustion, and comprising a container (37) which has an inlet (38) for sulphur-dioxide-containing gas from the combustion device (32); an outlet (39) for cleaned gas (40); means (41, 42, 43) for supplying, circulating and finely dividing an aqueous solution, whose  
35 pH is adjusted by the addition of an alkaline solution or alkaline substance, so as to contact it with the sulphur-dioxide-containing gas

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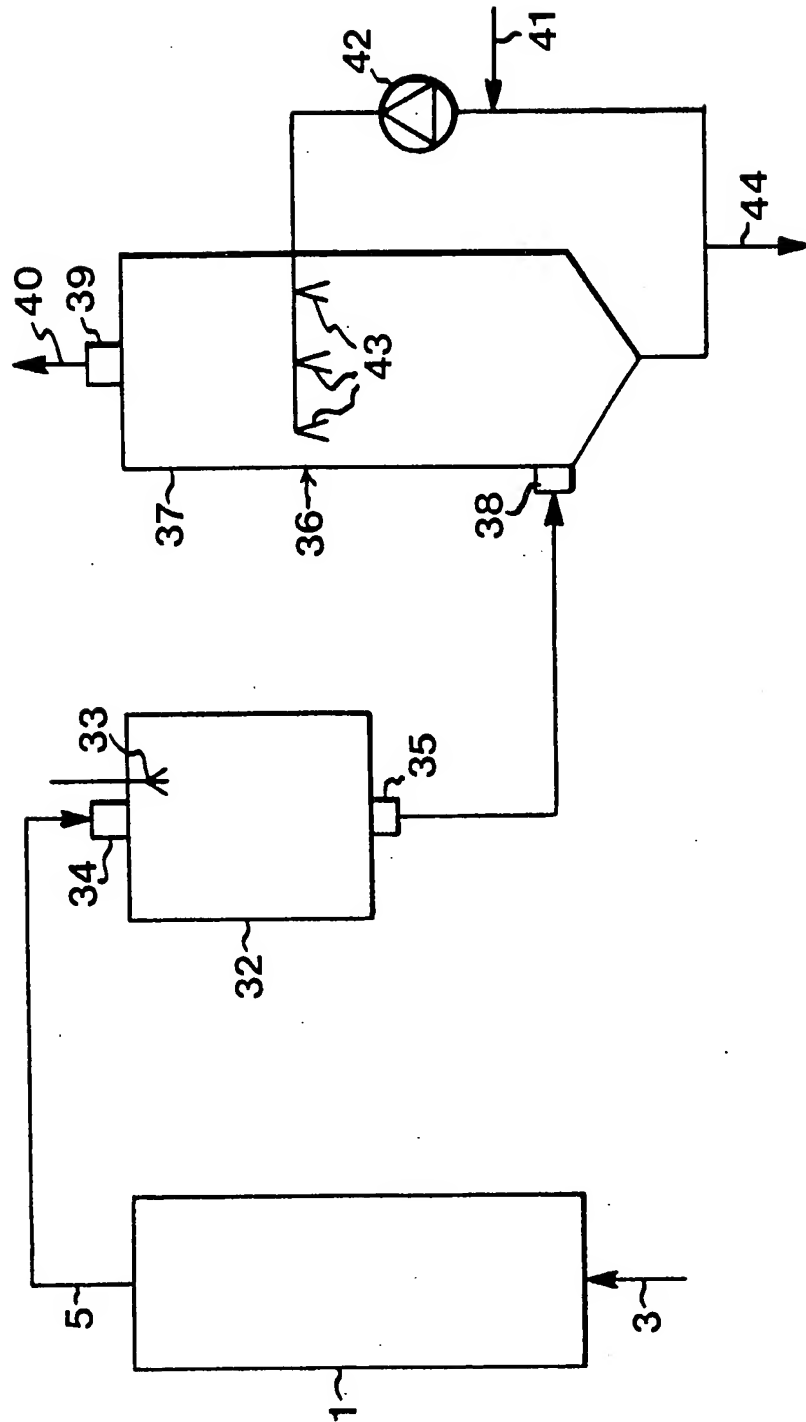
supplied; and means (44) for discharging solution that has absorbed sulphur dioxide.





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FIG.2



1  
INTERNATIONAL SEARCH REPORT

International application No.  
PCT/SE 94/00829

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01D 53/14, B01D 53/52, B01D 53/78, D21C 11/12 // D21C 11/08, D21C 11/06  
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01D, D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	SE, A, 9300533 (ABB FLÄKT AB), 19 August 1994 (19.08.94), claims 1-10, abstract --	1-10
P,X	WO, A1, 9325751 (COMBUSTION ENGINEERING, INC.), 23 December 1993 (23.12.93), page 14, line 26 - line 36; page 16, line 9 - line 27; page 17, line 4 - line 14 --	1-10
P,X	SE, B, 470516 (CHEMREC AB), 27 June 1994 (27.06.94), page 2, line 10 - line 19, figure 1 --	1-10

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

- \* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

14 December 1994

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Date of mailing of the international search report

19 -12- 1994

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 94/00829

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

26/11/94

International application No.

PCT/SE 94/00829

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WO-A1- 9325751	23/12/93	NONE	
SE-B- 470516	27/06/94	SE-A- 9203297	06/05/94
SE-B- 448173	26/01/87	CA-A- 1272005 EP-A,B- 0223821 SE-T3- 0223821 JP-B- 3043393 JP-T- 62503110 SE-A- 8502731 US-A- 4808264 WO-A- 8607396	31/07/90 03/06/87  02/07/91 10/12/87 04/12/86 28/02/89 18/12/86